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THE CHANGE IN ADSORPTION PROPERTIES OF ENZIMATICALLY MODIFIED POLYESTER

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It is known that alkaline hydrolysis of poly(ethylene-terephthalate) fabric (PET) improves the aesthetic appearance and comfort, but it is not environmentally friendly. Enzymes are biodegradable, non-toxic, degrade certain substance, reducing processing time and save energy. Since the possibility of adsorption depends on the number of available groups, the effects of PET fabric enzymatic hydrolysis were investigated in this paper. The lipase enzymes produced in the laboratory and a mixture of commercial lipases *Lipomod™ 299P* i *Lipomod™ 29P* from the company Biocatalysts were applied. The change in adsorption properties was monitored by adsorption of Fluorescent Brightener 135 – benzoxazole derivative applied in three concentrations and by the determination of moisture management ability on a Moisture Management Tester according to AATCC TM 195-2017. The results were compared with the untreated PET fabric and the reference sample (alkaline hydrolyzed PET fabric). From the results of spectral remission, fabric whiteness according CIE, tint deviation and tint value, the concentration of 1.2 % owf of optical brightener was determined to be optimal. Enzymatically hydrolyzed fabrics achieved slightly weaker adsorption and hydrophilicity effects than alkaline hydrolysis, but still significantly better than untreated PET fabric. The results of MMT, especially the values for Accumulative one-way transport capacity (R), confirm that.

Keywords: Polyester hydrolysis, Lipase, Optical brightening, MMT, Adsorption

INTRODUCTION

At this time when recycling is very significant, fibers from synthetic polymers became very important materials in the textile industry. Poly (ethylene terephthalate) (PET) is the most widely used synthetic fiber. However, PET also has disadvantages, most of which can be attributed to low hydrophilicity which causes difficulties in finishing, washing and dyeing. In addition, due to the accumulation of electrostatic charge and peeling on the surface of PET fabrics, it reduces the comfort of clothing [1-3]. There have been many attempts to modify the surface of PET materials for low hydrophilicity. It is known that alkaline hydrolysis of PET fabric improves the aesthetic appearance and comfort, but it is not environmentally friendly. Enzymatic modifications of PET fibers have been shown to be an alternative to chemical treatment with alkalis and amines [1, 3, 4]. Enzymatic hydrolysis is more favorable than conventional chemical hydrolysis of alkalis because it consumes less energy and does not require hazardous chemicals. Advantages of enzyme application instead of conventional chemicals is that they are environmentally friendly, biodegradable, non-toxic, have a specific degradation of certain substance, reduce processing time and save energy, improve material coloration, and are relatively cheaper due to increasing mass production. Moreover, enzymatic hydrolysis is limited to the surface of the fibers because the enzymes cannot penetrate the fiber, so there is no reduction in fiber strength. Some of the enzymes that can be applied to PET fabric hydrolysis include lipases, cutinases, and esterase. These enzymes hydrolyze ester bond of PET, forming new hydroxyl and carboxyl groups on the fiber surface, which increases the hydrophilicity of PET fabric. Among them, lipases have the largest number of industrial applications and are already considered effective enzymes for the hydrolysis of PET fabrics [1, 3, 5-9]. Since the possibility of adsorption of water, dyes or optical brighteners depends on the number of available groups, the change in adsorption/hydrophilicity of PET fabric after enzymatic hydrolysis were investigated in this paper.

EXPERIMENTAL PART

In this research polyester fabric (Incel, Banja Luka), made of 100% poly (ethylene-terephthalate), PET, was used. The fabric was woven of textured multifilament yarns fineness 50 dtex (16f), having mass per unit area 60 g/m^2. Surface of PET was modified by lipase enzymes that were produced in the laboratory and a mixture of commercial lipases *Lipomod^{TM} 299P* i *Lipomod^{TM} 29P* from the company Biocatalysts. Labaratory enzymes of the lipase type from the culture of the microorganism *Penicililluium sp.* OIL 1 were insulated from air according to Đorđević and collaborators [6]. Labels and surface modifications are presented in Table 1.

Table 1: Labels and treatment of PET fabrics

Label	Treatment/surface modification
PET	Untreated PET fabric
PET-AH	Alkali hydrolyzed PET fabric
PET-EH	Enzimatic hydrolysis with lipase from *Penicililluium sp.* OIL 1
PET-LH	Enzimatic hydrolysis with mixture of commercial lipases *Lipomod^{TM} 299P* and *Lipomod^{TM} 29P*
-conc.	Optical brightening in three concentrations (1.2; 2.4 and 4% owf)

The polyester fabric was hydrolyzed with 1.5 mol/l NaOH at a bath ratio, LR 1:100, at 100 °C, 60 min with horizontal stirring at 110 rpm. After processing, the fabric was rinsed with hot distilled water for 40 s, washed twice with cold distilled water, neutralized with 1 % CH_3COOH, rinsed until neutral and air dried.
Uvitex ERN-P (Fig. 1), an optical brightener for polyester – benzoxazole derivative (Fluorescent Brigthener 135, C.I. 45152), was applied in three concentrations (1.2; 2.4 and 4% owf) by batch wise method in stainless-steel bowls (Linitest, Original-Hanau). Processing conditions were LR 1:50 at 100 °C for 30 min.

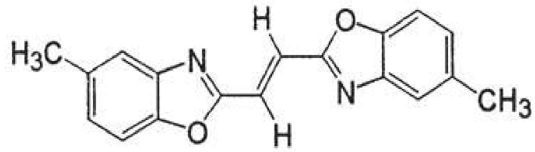

Figure 1: Uvitex ERN-P (Ciba), Fluorescent Brigthener 135, C.I. 45152 [1]

The adsorption properties were monitored by adsorption of optical brightener and determination of moisture management ability on a Moisture Management Tester (MMT M290), SDL Atlas, according to AATCC TM 195-2017 *Liquid Moisture Management Properties of Textile Fabrics*.
Spectral remission was measured on a remission spectrophotometer Spectraflash SF 300 (Datacolor) and the fabric whiteness (W_{CIE}) according to ISO 105-J02:1997 *Textiles - Tests for colour fastness - Part J02: Instrumental assessment of relative whiteness*, tint deviation (TD) and tint value (TV) were calculated automatically.

RESULTS AND DISCUSSION

The hydrophilicity of enzymatically hydrolyzed PET fabric was researched in this paper. For this purpose, PET fabric was hydrolyzed with NaOH, laboratory-made enzymes and commercial enzymes, a mixture of lipases, *Lipomod™ 299P* and *Lipomod™ 29P*. The adsorption of Uvitex ERN-P optical brightener and the ability to manage moisture were tested on such hydrolyzed PET fabrics. The results of enzymatic hydrolysis were compared with the untreated sample and the reference alkaline hydrolyzed PET fabric.
Spectral characteristics of the fabric are expressed through remission, R [%], degree of whiteness according to CIE, W_{CIE}, and deviation of tone from ideal white, TD. The results are shown in Table 2 and in Fig. 2-5.
The results of the spectral characteristics show that the untreated PET fabric has a remission of 78.94 at 700 nm and a degree of whiteness of 71.7 without a noticeable deviation of tone from the white standard. It can be seen from the remission curve that all wavelengths are equally represented. Hydrolysis cleans the surface, but depending on the means by which the hydrolysis is carried out, the effects differ. Alkaline hydrolysis (PET-AH) increases whiteness to 72.8, but there was no remission. Enzymatically hydrolyzed PET fabrics show similar remission, but the whiteness is slightly lower W (PET-EH) = 64.20, W (PET-LH) = 67.90. It is evident that enzymatic treatments did not result in the same surface cleaning as alkali. Slightly better results, more similar to alkaline hydrolysis, were achieved with commercial lipases (PET-LH). The shift of tone occurred towards the blue-green area, which is visible from the remission curves because the remission decreased at 590 nm.

Table 2: Values of maximum remission and wavelength at which it is achieved, degree of whiteness and tint value and tint deviation of the color tone from the ideal white standard of polyester fabric after hydrolysis and optical brightening with Uvitex ERN-P

Fabric	R_{max} [%]	λ_{max} [nm]	W_{CIE}	TV	TD
PET	78.94	700	71.70	-0.20	/
PET-AH	78.95	700	72.80	0.20	/
PET-EH	78.66	700	64.20	-0.60	R1
PET-LH	79.01	700	67.90	-0.40	/
PET-1.2	97.23	440	118.91	1.10	G1
PET-AH-1.2	101.39	440	125.00	1.60	G2
PET-EH-1.2	98.24	440	125.20	1.40	G1
PET-LH-1.2	96.91	440	121.30	3.00	G3
PET-2.4	98.00	450	122.40	3.00	G3
PET-AH-2.4	100.47	440	125.90	2.00	G2
PET-EH-2.4	96.41	450	122.80	3.30	G3
PET-LH-2.4	98.40	440	123.40	2.50	G3
PET-4.0	97.96	450	116.00	4.80	G5
PET-AH-4.0	96.61	450	117.60	3.10	G3
PET-EH-4.0	94.05	450	115.30	4.60	G5
PET-LH-4.0	96.96	450	117.20	3.80	G4

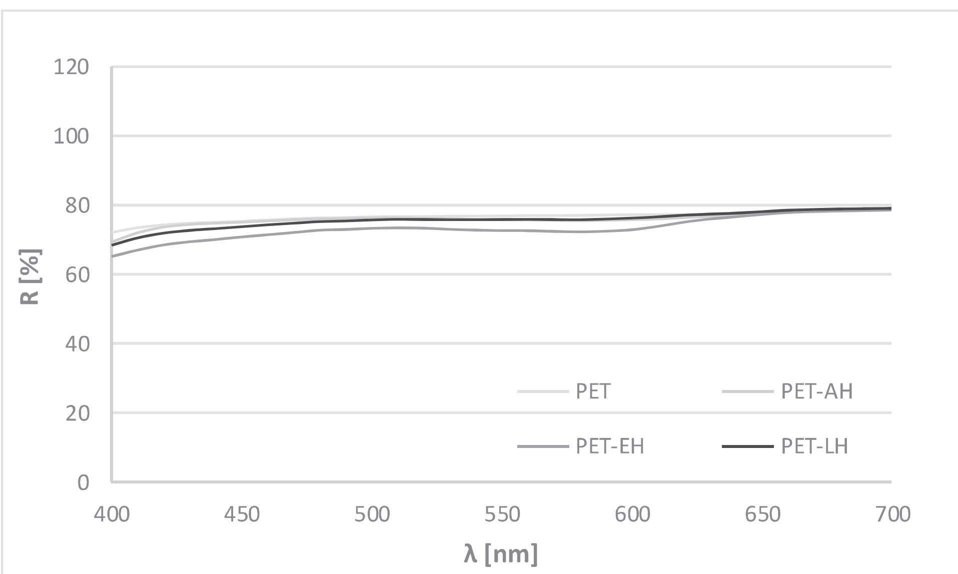

Figure 2: Remission curves of polyester fabric after hydrolysis

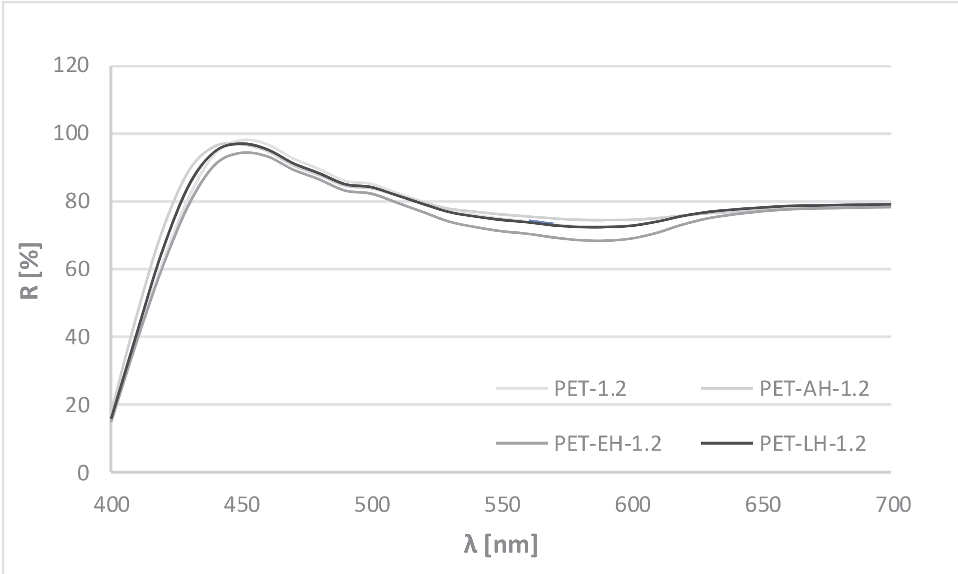

Figure 3: Remission curves of polyester fabric after hydrolysis and brightening with optical brightener Uvitex ERN-P concentration 1.2%

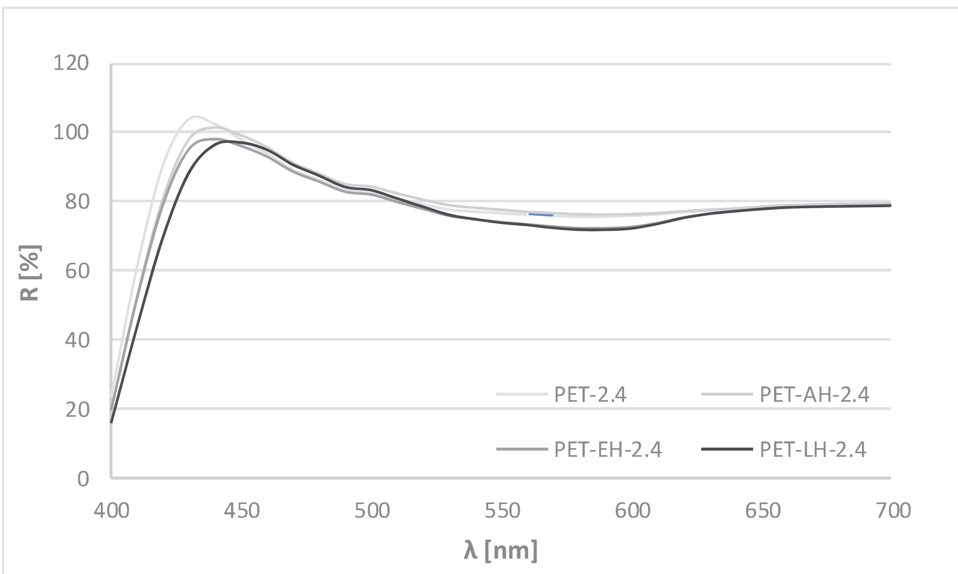

Figure 4: Remission curves of polyester fabric after hydrolysis and brightening with optical brightener Uvitex ERN-P concentration 2.4%

The possibility of adsorption of water, dyes or optical brightener depends on the number of available groups. To determine the adsorption capacity of PET fabrics after hydrolysis, optical brightener was applied in three concentrations proposed in the literature for Fluorescent Brightener 135 (Ciba) using the depletion method [10]. From all remission curves, the characteristic peak for fluorescence at 440 nm and 450 nm at higher concentrations is clearly visible. It has been shown that very high degree of whiteness is achieved by applying the lowest concentration of optical brightener of 1.2%. PET fabric treated with 1.2 % optical brightener has a whiteness degree of W = 118.9.

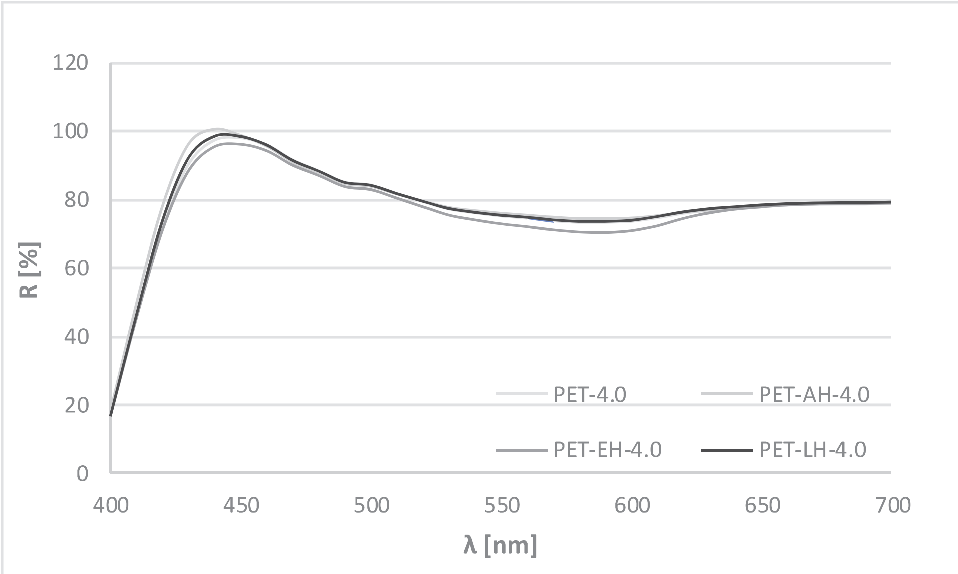

Figure 5: Remission curves of polyester fabric after hydrolysis and brightening with optical brightener Uvitex ERN-P concentration 4.0%

It is lost in mass by hydrolysis [10], but it can be seen that the whiteness still increased significantly from whiteness level 70 to 125. By modifying the fiber surface, the adsorption surface area is increased to increase the number of surfactant groups. For this reason, the hydrolyzed surfaces adsorbed a larger amount of optical brightener leading to better fabric whiteness. PET fabric treated with 2.4 % optical brightener has W = 122.4. The alkaline hydrolyzed PET fabric, PET-AH, still has a higher degree of 125.9, indicating better adsorption. Comparing enzymatically treated PET with unmodified and alkali hydrolyzed, it is seen that a similar degree of whiteness is achieved as with alkaline hydrolysis, but this modification is much more environmentally friendly. In addition, it can be seen that the degree of whiteness after enzymatic hydrolysis is lower, and reaching a similar degree later indicates better depletion because 4-5 degrees of whiteness of the difference are compensated. With the increase in the concentration of optical brightener, the spectral remission also increased, but by exceeding the concentration of the so-called optimal, spectral remission is reduced. Treatment with the lowest concentration of optical brightener Uvitex ERN-P 1.2 % achieves the highest degree of whiteness due to fluorescent remission at 440 nm. Already by treatment at a concentration of 2.4 % there is a visible deviation of the shade from the white standard; the fabrics become clearly green. With increasing concentration, the change in tone is even stronger, so that 4 % leads to a very green tone. There is a significant shift towards the blue-green area which is accompanied by a shift of the maximum remission from 440 to 450 nm. All fabrics record the same behavior, and it is recommended to use lower concentrations of optical brightener because the occurrence of concentration quenching of fluorescence has occurred. Namely, increasing the concentration of optical brighteners does not mean increasing the degree of whiteness, on the contrary, there is a limit concentration to which an increase in whiteness is achieved, but exceeding the limit concentration of whiteness decreases, and materials take on a different shade. The concentration limit recommended for optical brightening is specific to each optical brightener and depends on the type of material on which it is applied [11]. The three main causes of reduced whiteness when using excessive concentrations are partial absorption of visible light, shift of the fluorescence spectrum towards longer wavelengths, and concentration quenching of fluorescence.

According to the results, it is visible that increasing the concentration of optical brightener also increases the spectral remission, but by exceeding the concentration from the optimal one, the spectral remission decreases. When using 4% optical brightener Uvitex ERN-P, concentration quenching of fluorescence is observed (reduction of whiteness and remission, shift towards green). This can be explained by the excessive concentration of optical brightener molecules on the fabric. The layering of optical brightener molecules cannot excite all the layers and therefore there is no fluorescence that directly affects the reduction of whiteness. Additionally, optical brightener molecules at high concentrations build dimers that do not have the ability to fluoresce.

The ability to manage the liquid moisture of PET fabrics after hydrolysis was determined according to AATCC 195-2017 Liquid Moisture Management Properties of Textile Fabrics on the Moisture Capability Testing Device (MMT). The results are collected in Table 3.

Table 3: Moisture management properties of hydrolized PET fabrics

Fabric		PET		PET-AH		PET-EH		PET-LH	
		Mean	*CV	Mean	*CV	Mean	*CV	Mean	*CV
WT [s]	T	0.187	0	3.931	0.9781	2.027	0.8787	1.029	0.7101
	B	0.187	0	4.118	0.9084	2.745	0.0788	0.998	0.7038
AR [%/s]	T	16.755	0.0592	32.166	0.5654	9.124	0.0839	11.712	0.2335
	B	32.743	0.1472	55.711	0.3768	60.102	0.033	49.732	0.1241
MWR [mm]	T	23.333	0.1237	10	0	13.333	0.2165	25	0.2000
	B	26.666	0.1083	10	0	21.666	0.3525	26.666	0.1083
SS [mm/s]	T	20.698	0.0078	1.364	1.5049	9.171	0.8629	14.602	0.3058
	B	20.824	0.0138	1.312	1.5091	4.536	0.3312	12.627	0.5085
R [%]		430.391	0.0685	693.918	0.1459	687.17	0.0149	558.574	0.0928
OMMC		0.813	0.0165	0.653	0.0725	0.858	0.0658	0.860	0.0199
Type of fabric		*Moisture Management Fabric*		*Water Penetration Fabric*		*Moisture Management Fabric*		*Moisture Management Fabric*	

*Wetting Time - WT, Absorption rate -AR, Maximum wetted radius - MWR, Spreading speed - SS, top surface – T, bottom surface – B, Accumulative One-way Transport Capability – R, Overall (liquid) Moisture Management Capability – OMMC, *CV – coefficient of variation*

The wetting time measured on the MMT is the time period in which the upper and lower surface of the fabric are just beginning to wet [12]. From the results shown in Table 3 it can be seen that the untreated fabric has an extremely short wetting time, WT, and a large wetting radius indicating a hydrophobic surface of high capillarity. Hydrophobic PET would be expected to have no wetting time. However, the main difference between PET film and PET fabric has to be pointed: in case the film surface is homogeneous, whilst the fabric has a heterogeneous surface due to the intrayarn and interyarn porosity [13, 14]. In the case of hydrolyzed PET fabrics, the wetting time is 4 s for alkaline and 2 s for enzymatically hydrolyzed fabric. The reason is surface change and better absorption, so a small amount of water binds to new surface groups of PET fibers. Therefore, the lower rate of PET absorption is significantly higher for hydrolyzed PET fabrics.

The absorption rate represents the average rate of liquid moisture absorption for the upper and lower surface of the sample during the initial change in water content during the test. The rate of expansion, which is the accumulated surface wetting rate from the center of the sample at which the discharge solution descends to the largest wet radius, is faster on the hydrophobic surface of untreated PET (20.7 mm/s) than on hydrolyzed PET (AH 1.3 mm/s, EH 9 mm/s and LH 14 mm/s), which suggests higher capillarity of untreated PET, but at the same time better absorption of hydrolyzed PET fabrics. Accumulative one-way transport capacity (R) represents the difference between the range of liquid moisture content curves of the upper and lower surface of the sample with respect to time. If the water content on the upper surface is much higher than on the lower, the absorption is higher. For untreated PET fabric R is 430%, and for hydrolyzed AH 693 %, EH 687% and LH 558 %. Thus, hydrolyzed PET fabrics have a higher R and better absorption effect than untreated ones. Total (liquid) moisture management capacity (OMMC) is calculated by combining three measured properties: the rate of liquid absorption at the bottom surface, the one-way ability to transfer liquid, and the maximum rate of moisture spreading at the bottom surface. It represents an index of the overall ability of the fabric to transport liquid moisture. Based on the results, MMT classifies fabrics [12]. For untreated PET fabric OMMC is excellent which suggests a moisture management fabric, while for alkaline hydrolyzed it is very good, which indicates a water penetration fabric. However, enzymatically hydrolyzed fabrics retain this property, and excellent OMMC which suggests a moisture management fabric.

CONCLUSION

Considering the results, the concentration of 1.2 % owf of optical brightener was determined to be optimal. At higher concentrations, fluorescence is quenched, resulting in a shift of hue to blue-green (batochromic shift). Enzymatically hydrolyzed fabrics achieved slightly weaker adsorption and hydrophilicity effects than alkaline hydrolysis, but still significantly better than untreated PET fabrics. The results of MMT confirm that, especially the values for Accumulative one-way transport capacity (R). Since hydrolyzed PET fabrics have a higher R, the water content on the upper surface is much higher than on the lower one, clearly indicating better absorption than of untreated PET fabric.

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